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Corrugation in the Nitrogen-Graphite Potential Probed by Inelastic Neutron Scattering

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Inelastic neutron spectra of the commensurate $\sqrt{3}\times 3$ herringbone monolayer phase of nitrogen physisorbed on the graphite (002) surface at low temperature have been compared with lattice-dynamics calculations of the polycrystalline-averaged one-phonon coherent neutron cross section. The observed zone-center energy gap of $\sim$0.4 THz in the acoustic-phonon branches is a factor of 2 larger than calculated from central atom-atom potentials. We conclude that current models of the corrugation in the adatom-substrate potential greatly underestimate the lateral restoring forces in this relatively simple molecular film.

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The structure and phase transitions of physisorbed films, particularly on graphite basal-plane surfaces, have been extensively studied for over fifteen years. In many cases, the structure of these systems reflects a delicate balance between intermolecular interactions and the lateral periodic variation of the adatom-surface potential, the so-called corrugation in the holding potential.[1,2] Future advances in understanding the structure of monolayer solids as well as the character of their phase transitions will likely depend on better knowledge of the corrugation in the holding potential.

The adatom-substrate corrugation of physisorbed films has proved to be very difficult to determine experimentally. Molecular scattering has been useful; but, for graphite surfaces, such work has been largely limited to He-atom scattering. Most of our knowledge of the corrugation for adsorbates on graphite is based on semiempirical atom-atom potentials.[3] However, even for a rare gas such as Kr on graphite, these potentials fail to account for the observed commensurate monolayer phase.[4] Here we shall show that they also greatly underestimate the energy gap in the acoustic-phonon branches of a simple molecular film, nitrogen adsorbed on graphite. This result demonstrates that the corrugation implied by these potentials cannot account for the lateral restoring forces present in the commensurate monolayer even though its structure is predicted correctly.

On a smooth surface with no corrugation in the holding potential, the acoustic phonons of a crystalline monolayer have zero frequency at the Brillouin zone center. Such zero-wave-vector modes correspond to a uniform translation of the entire monolayer. On the other hand, if the monolayer is commensurate with the substrate (or nearly so), the corrugation in the potential provides a restoring force for the adatoms. The resulting translational modes have a nonzero frequency usually referred to as the zone-center gap. At low temperature, the gap frequency reflects the curvature of the adatom-substrate potential at the equilibrium atomic positions. Recently, inelastic neutron scattering (INS) has been used to investigate the zone-center gap in the phonon spectrum of a physisorbed monolayer. Frank and co-workers[5,6] obtained INS spectra for the $\sqrt{3}\times\sqrt{3}$ commensurate phase of D_2 on graphite. From these they inferred a gap for the lowest-energy modes which is 10% larger than the value from the quantum self-consistent phonon calculations of Novaco.[7]

We have undertaken both INS experiments and lattice-dynamics calculations for a commensurate monolayer of N_2 physisorbed on the graphite (002) surface. The structure and phase transitions of this simple molecular monolayer system have been extensively studied

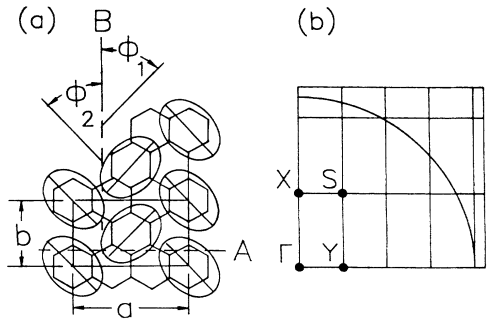

FIG. 1. (a) Projection of the commensurate N_2-monolayer unit cell on the graphite (002) surface. The cell dimensions are $a=7.38$ Å ($=3a_g$) and $b=4.26$ Å ($=\sqrt{3}a_g$), where $a_g=2.46$ Å is the graphite lattice constant. The N−N bond of the molecules is parallel to the surface. (b) Reciprocal lattice of the N_2 monolayer in the repeated-zone scheme showing an arc of radius $Q=1.70$ Å^{-1}.

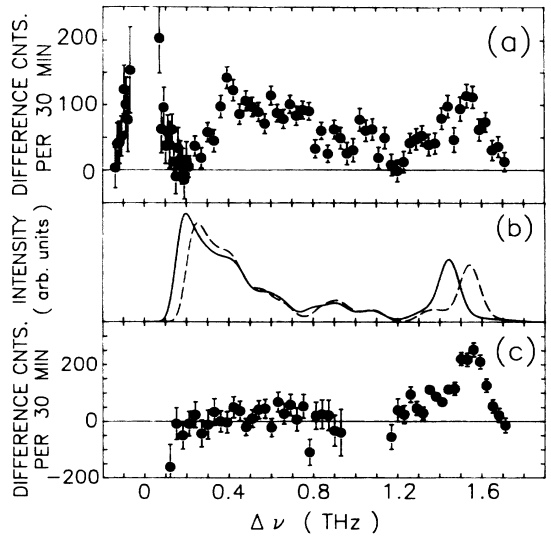

FIG. 2. (a) Neutron energy-loss spectrum from the N_2 monolayer taken at 4 K with $Q=1.70$ Å^{-1} directed parallel to the Papyex sheets. The elastic peak $\Delta\nu=0$ has been truncated. (b) Calculated one-phonon inelastic coherent cross sections after spherical averaging and folding with the instrumental resolution function. Two different N_2-graphite potentials were assumed: isotropic atom-atom (C-N) potential of Ref. 20 (solid curve), and anisotropic atom-atom potential of Ref. 26 (dashed curve). (c) Neutron energy-loss spectra from the N_2 monolayer taken at 4 K with **Q** perpendicular to the Papyex sheets: $Q=1.70$ Å^{-1} ($\Delta\nu<1.0$ THz) and $Q=2.25$ Å^{-1} ($\Delta\nu>1.0$ THz).

both theoretically[8-10] and experimentally.[11,12] However, despite detailed lattice-dynamics calculations,[13] there have been no previous experimental investigations of the phonon spectra of this system.

The INS experiments were performed on the triple-axis spectrometer IN3 at the Institut Laue-Langevin reactor by the same technique used in the D_2 monolayer experiments.[5,6] The spectrometer was operated in an energy-loss, fixed-final-energy configuration ($E_F=5.04$ meV) with a horizontally focusing analyzer giving an elastic resolution of 0.07 THz full width at half maximum (FWHM) and increasing to 0.12 THz FWHM at an energy transfer of 2 THz. The sample cell was filled with Papyex[14] sheets which could be mounted so that the majority of graphite c axes were either parallel or perpendicular to the wave-vector transfer **Q** (denoted parallel and perpendicular configurations, respectively). The commensurate monolayer corresponded to a coverage of 202-cm^3 STP of N_2, and all spectra were taken at a temperature of 4 K.

The unit cell of the commensurate $\sqrt{3}\times3$ herringbone monolayer phase is shown in Fig. 1(a). As a result of the presence of the glide lines labeled A and B,[11] the azimuthal angles ϕ_1 and ϕ_2 are equal. From neutron diffraction measurements,[12] these angles have been determined to be in the range 40°–50°. Figure 2(a) shows the INS spectrum taken at wave-vector transfer $Q=1.70$ Å^{-1} in the parallel configuration. This Q value was chosen to give a good sampling of the region of reciprocal space near the center of the Brillouin zone as shown in Fig. 1(b).[15] The background scattering from the Papyex substrate has been subtracted. It is evident that the spectrum is dominated by two peaks at ~0.4 and 1.5 THz. These peaks reproduced in two other spectra taken under the same conditions; there were no other discernible features up to 2.5 THz. The width of the elastic peak (at 0 THz) is the same as the instrumental ble to determine whether there are any other energy-loss peaks below 0.2 THz.

In an effort to determine the polarization of the vibrational modes near 0.4 and 1.5 THz, shorter scans were made in the Q-perpendicular configuration. As shown in Fig. 2(c), it is now very difficult to resolve any peaks in the spectrum near 0.4 THz, and the peak at 1.5 THz is enhanced. These features are consistent with assigning the lower-frequency modes to atomic displacements parallel to the graphite surface and the upper modes to displacements perpendicular to the surface.[16]

Our modeling of the neutron spectra in Fig. 2 is performed on a film structure at zero temperature determined by minimizing the energy of a monolayer cluster including the molecular zero-point energy.[17] The basic intermolecular interaction is the $X1$ model of Murthy, Singer, and McDonald[18] supplemented by the McLachlan substrate-mediated interaction[19] and Steele's model of the N_2-graphite interaction.[20] Our procedure differs slightly from that of Cardini and O'Shea[13] who neglected the McLachlan interaction and the molecular zero-point energy and used a different molecular quadrupole moment.

The calculated structure[17] reproduces the observed $\sqrt{3}\times3$ registry of the N_2 monolayer on the graphite (002) surface [Fig. 1(a)][11] and yields an in-plane her-

ringbone arrangement of the molecules having an azimuthal angle $\phi \simeq 45°$ within the range inferred experimentally.[12] The calculated height of the molecules above the surface is 3.39 Å compared to the Cardini and O'Shea value of 3.32 Å based on the classical potential energy. The molecular height has not been determined experimentally.

Once the film structure was found, we performed harmonic lattice-dynamics calculations to obtain its phonon spectrum. The dynamical calculations omit the McLachlan substrate interaction and the stretching of the intramolecular N−N bond (at a much higher frequency than the lattice vibrations). A molecule's configuration is described by its center-of-mass position and the polar and azimuthal angles of its N−N bond; each molecule has five degrees of freedom, and there are two molecules per unit cell. The ten branches of the dispersion relations are shown in Fig. 3(a) for selected symmetry directions in the Brillouin zone along with the calculated phonon density of states in Fig. 3(b).

We have calculated the one-phonon inelastic coherent cross section for neutrons scattered inelastically from the polycrystalline monolayer.[21] The results, after folding with the instrumental energy resolution function, are shown in Fig. 2(b) for two different models of the N_2-graphite holding potential. In order to represent the polycrystalline nature of the film, the cross section has been spherically averaged over all possible orientations of the film lattice with respect to the wave-vector transfer **Q**.[22] However, preferential orientation of the crystallites in the Papyex substrate affects the experimental mode intensities as shown in Fig. 2(c). Since our main concern is calculating the mode frequencies rather than their intensities and the frequencies are independent of the type of averaging, spherical averaging of the cross section is sufficient for our purpose here.

The predicted spectra in Fig. 2(b) are qualitatively similar to the observed spectrum in Fig. 2(a). The solid curve, computed for the interaction model described above, is dominated by peaks at ~0.2 and 1.45 THz. Polarization analysis reveals that the 1.45-THz peak is the almost dispersionless bouncing mode of the molecules normal to the surface while that at 0.2 THz is associated with the lowest longitudinal- and transverse-acoustic modes polarized parallel to the surface. These identifications are consistent with the upper peak persisting and the lower one diminishing in the out-of-plane scattering configuration [see Fig. 2(c)].[16] As in the observed spectrum, the lower peak is asymmetric and has some structure in its high-frequency tail. For our purposes, it is important to note that the maximum in intensity at 0.2 THz results from the flat region of the dispersion curves near the Brillouin-zone center so that its frequency accurately reflects the calculated magnitude of the zone-center gap.

The most striking difference between the observed and

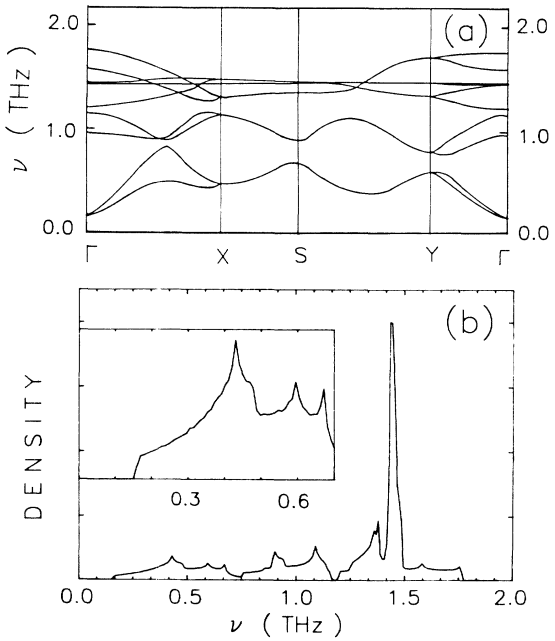

FIG. 3. (a) Phonon dispersion relations of the N_2 monolayer calculated for selected symmetry directions in the Brillouin zone using the isotropic adatom-substrate potential. (b) The corresponding phonon density of states of the N_2 monolayer.

calculated spectra is that the lower peaks occurs at ~0.4 THz rather than the ~0.2 THz predicted. To increase substantially the calculated zone-center gap requires an increase in the effective corrugation of the N_2-graphite potential.[23] One method to accomplish this is to use anisotropic atom-atom potentials[24] similar to those which have been found to give a larger corrugation for rare gases adsorbed on graphite than do isotropic potentials.[25] We calculated the dashed curve in Fig. 2(b) for the Joshi-Tildesley anisotropic model of the N_2-graphite interaction.[26] It can be seen that the calculated peak from the zone-center modes is now at 0.26 THz but still well below that observed; the agreement with the bouncing mode at 1.5 THz has improved.

From an experimental standpoint, it is important to appreciate that the peak in the INS spectrum contributed by the zone-center modes arises from the coherent character of the scattering. If an incoherent scatterer is used instead, the one-phonon cross section is an average over the entire Brillouin zone[6,22] rather than the single arc in Fig. 1(b) which preferentially samples the zone center. The one-phonon incoherent cross section then more closely resembles the density of states [Fig. 3(b)] which has a shoulder rather than a peak at the zone-center gap frequency.[6,22]

To conclude, we have identified a peak in the INS spectra of a commensurate N_2 monolayer on graphite whose frequency accurately measures the zone-center gap in the lowest acoustic-phonon branch. The inferred

gap frequency is a factor of 2 larger than present models predict. This discrepancy shows that current models of the adatom-substrate potential give a poor representation of the corrugation for this relatively simple and widely studied molecular film and suggests that further work is required to improve model potentials for prototypical physisorbed monolayers.

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